Headspace Solid Phase Microextraction/Gas Chromatography for Determination of Aldehydes

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and Pichan Chiamchunkoop1

ABSTRACT

A headspace solid-phase microextraction (HS-SPME) procedure was developed for the determination of aldehydes. The aldehydes were derivatized to form oxime with O-2,2,4,5,6-(pentafluoro-benzyl) hydroxylamine (PFBHA), prior to the extraction using HS-SPME and analyzed by gas chromatograph-flame ionization detector. The optimum condition for HS-SPME was studied. It was found that the acceptable results were obtained when 0.50 g of NaCl was added into 4.00 mL of aqueous sample, followed by 0.50 mL of 1000.0 ppm PFBHA solution, stirred for 5 minutes, and then extracted at room temperature for 10 minutes with a PDMS/DVB coated fiber. The fiber was then desorbed at 250°C for 5 minutes and analyzed by GC-FID. The external standard calibration curves showed good linearity ($R^2 > 0.995$) over the range of 0.5-1000 ppb for formaldehyde; 1.0-700 ppb for acetaldehyde, propanal, butanal and hexanal; and 1.0-500 ppb for heptanal. Detection limits and quantification limits varied from 0.0005 to 1.0 ppb and 0.5-1.0 ppb, respectively. This method was applied to the analysis of aldehydes in the seafood immersed water samples. Formaldehyde and acetaldehyde were found in these samples in the concentration range of 13-31 ppb and 33-179 ppb, respectively. The relative standard deviations (RSD) and the recoveries of the analyses ranged from 0.6 %-3.3 % and 96.5%-105.3% were obtained, showing that the precision and accuracy of this method are good.

Key words: low molecular weight aldehyde, solid phase microextraction

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INTRODUCTION

In recent years, aldehydes are receiving increasing attention as disinfection and oxidation by-products formed during drinking water treatment processes, especially those with low molecular weights. Formaldehyde is classified as a human carcinogen that causes nasopharyngeal cancer and probably leukemia, and acetaldehyde induces tumors; propanal, butanal, pentanal, hexanal, nonanal, glyoxal, methyl glyoxal are mutagens in laboratory animals. Besides the health affects mentioned above, these aldehydes may also cause taste and odor problems in drinking water (Shih and Chun, 2003). Analysis of aldehydes in water is very difficult due to low concentrations and high polarity, derivatizations prior to their detection by a chromatographic or spectroscopic technique are widely performed for the low-molecular-weight aldehydes. For example, derivatization with 2,4-dinitrophenylhydrazine (2,4-DNPH) followed by liquid-liquid extraction (LLE) has been used by the US Environmental Protection Agency (US EPA). The 2,4-DNPH method potentially allows specific quantitation of different aldehydes and ketones through high performance liquid chromatography (HPLC)/ ultraviolet (UV) detection of their hydrazones but not by gas chromatography (GC) since many hydrazones decompose at high temperatures (Tsai and Chang, 2002). Another commonly used method for determining aldehydes is based on derivatization with O-2,3,4,5,6-(pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA). PFBHA reacts with carbonyls to form the corresponding oximes. PFBHA method has also been suggested by both the US EPA and the US American Public Health Association (APHA). All the methods mentioned above involve complex procedures for sample preparations and therefore very time-consuming (Cancilla and Que Hee, 1992). The technique called solid-phase microextraction (SPME) has been developed by Pawliszyn, (1999). SPME presents many advantages over conventional methods by combining sampling, preconcentration, and direct transfer of the analytes into a GC. Sampling and analysis method for aldehydes in air which combined PFBHA with SPME technique have been reported. For water sample, aldehydes derivatized with PFBHA to form oximes in solutions followed by extraction with SPME from liquid or headspace and analyzed by GC/ECD was also reported (Svensson et al, 2007). The research shown here reported another approach to determine the low molecular weight aldehydes; formaldehyde (C1), acetaldehyde (C2), propanal (C3), butanal (C4), hexanal (C6) and heptanal (C7) by derivatization with PFBHA followed by extraction of headspace aldehydes-PFBHA oximes using SPME fiber and analysis by GC/FID.

MATERIALS AND METHODS

Chemical and reagents

O-2, 3, 4, 5,6 (pentafluoro- benzyl) hydroxylamine hydrochloride, PFBHA was purchased from Sigma-Aldrich, and the 1000.0 ppm aqueous solution of PFBHA was prepared daily.
Formaldehyde (37 % in water) and sodium chloride were purchased from Ajax Finechem. Acetaldehyde (99.5 %) was purchased from Riedel-de Haen. Propanal, butanal, hexanal and heptanal were purchased from Fluka. Deionized water was purchased from the Government Pharmaceutical Organization. Stock of standard aldehydes 1000.0 ppm were prepared in deionized water and store at 4°C. Working standard solutions at different concentration were prepared by appropriate dilution.

Instrumentation

The GC/FID study was performed with Varian model CP-3800 gas chromatograph. Manual SPME Holder and PDMS/DVB fiber (65 μm) were purchased from Supelco.

GC/FID instrumental condition

The conditions were set as follows: temperature of injection port and FID were equally set at 250°C. A 30 m x 0.25 mm. id. CP SIL 8 CB with 0.25 μm film thickness was used for separation of aldehyde-PFBHA oximes. The carrier gas was helium with flow rate of 1.0 mL/min. The initial temperature of 50°C were ramped at 4°C/min to 220°C and 20°C/min to 250°C and the analysis time was 45 minutes. Helium was used as makeup gas with flow rate of 25 mL/min and H₂/Air flow at 30/300 mL/min.

Standard and sample preparations

The standard solutions or seafood immersed water samples were prepared by transferring 4.00 mL of solution, 0.50 mL of 1000 ppm PFBHA solution and 0.50 g of NaCl into a 10 mL headspace vial and immediately capped. The solution was stirred with magnetic stirrer for 5 minutes. The derivatization of aldehydes with PFBHA was performed to produce vaporized oximes in headspace area. Figure 1 shows a reaction scheme for the derivatization of aldehydes with PFBHA reagent to give two geometric isomers oxime products.[6]

Figure 1 Reaction scheme for the derivatization of an aldehyde with PFBHA to give cis- and trans-oxime isomers.
HS-SPME procedure

Before its first use the fiber was prepared by desorbing possible contaminants in the injection port of the GC for 30 min at 250 °C. The fiber was then exposed to a headspace of standard solution or seafood immersed water sample which were prepared according to the above procedure for 10 minutes. The fiber was then transferred immediately to the injection port of the GC and desorbed for 5 minutes at 250°C.

Optimum conditions studies

Standard solutions which were prepared according to the above procedure were used to study the effect of heating time (5-30 minutes), temperature of solution (room temperature, 50°C and 70°C), amount of NaCl (0.50 g, 1.00 g and 1.50 g), desorption time (3-10 minutes) in order to determine the optimum conditions for HS/SPME sample preparation.

Determination of aldehydes in real samples

These days, formaldehyde is used in order to prevent from spoiling, and to increase the storage time. Before putting on shelf, seafood is firstly dipped in formaldehyde–water solution for a period of time by dishonest mongers. The seafood dipped with formaldehyde is a big danger to the physical health of consumer. In this study, two of seafood immersed water samples were analyzed, the concentration of aldehydes in samples, the precision in the term of % relative standard deviations and the accuracy in the term of % recoveries were reported.

RESULTS AND DISCUSSION

Figure 2 showed typical GC/FID chromatogram of standard solution of aldehydes at concentration equaled 0.50 ppm. PFBHA was added and oximes of aldehydes were formed in solutions and vaporized to headspace by magnetic stirring. The headspace oximes were extracted with SPME fiber, desorbed in injection port of GC and separated in GC column. It was observed that there were cis and trans-isomers of the oximes because aldehydes were asymmetrical carbonyl compounds, except formaldehyde.
The influence of some parameters for HS-SPME sampling step were investigated and the results were shown in Figure 3-5. From the study, selected parameters for optimum conditions were as follows: NaCl 0.50 grams; extraction time, 10 minutes at room temperature; desorption time, 5 minutes.

Figure 3 Effect of amount of NaCl on peak areas of aldehyde-PFBHA oximes

Figure 4 Effect on extraction time and temperature on peak areas of aldehyde-PFBHA oximes.
(A) room temperature (28± 2 °C), (B) 50 °C and (C) 70 °C
Figure 5 Effect of amount of desorption time on peak areas of aldehyde-PFBHA oximes

Using the optimum conditions, determination of aldehyde levels in samples was performed with external standardization method. Good linearity and correlation coefficients were obtained. Detection limits and quantification limits varied from 0.0005 to 1.0 ppb and 0.5-1.0 ppb, respectively. In this study, two of seafood immersed water samples were analyzed. Recoveries were determined by spiking the sample with appropriate quantities of standard solutions. All relative standard deviations (%RSDs) observed are equal to or less than 3.3%. The results of analytical characters for this study and the result of analysis were shown in Table 1.

Table 1 Some analytical characters of HS-SPME/GC/FID obtained from this study and the quantification results

<table>
<thead>
<tr>
<th>Analytical character</th>
<th>Linear range (ppb)</th>
<th>Linear Equation</th>
<th>Linearity (R²)</th>
<th>LOD (ppb)</th>
<th>LOQ (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde (C₁)</td>
<td>0.5-1000.0</td>
<td>Y = 878.22 x +13822</td>
<td>0.9966</td>
<td>&lt;0.0005</td>
<td>0.5</td>
</tr>
<tr>
<td>Acetaldehyde (C₂)</td>
<td>1.0-700.0</td>
<td>Y = 106.08 X + 689</td>
<td>0.9954</td>
<td>&lt;0.0005</td>
<td>1.0</td>
</tr>
<tr>
<td>Propanal (C₃)</td>
<td>1.0-700.0</td>
<td>Y = 433.45 X + 2044</td>
<td>0.9984</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>Butanal (C₄)</td>
<td>1.0-700.0</td>
<td>Y = 298.51 X + 2657</td>
<td>0.9952</td>
<td>&lt;0.0005</td>
<td>1.0</td>
</tr>
<tr>
<td>Hexanal (C₆)</td>
<td>1.0-700.0</td>
<td>Y = 74.071 X + 872</td>
<td>0.9978</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>Heptanal (C₇)</td>
<td>1.0-500.0</td>
<td>Y = 33.038 X + 442</td>
<td>0.9974</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Concentration (ppb)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>C₁</td>
</tr>
<tr>
<td>Sample I</td>
<td>31.01</td>
</tr>
<tr>
<td>Sample II</td>
<td>13.31</td>
</tr>
<tr>
<td>% RSD (n=6)</td>
<td>1.1</td>
</tr>
<tr>
<td>%Recovery (n=3)</td>
<td>96.5</td>
</tr>
</tbody>
</table>
CONCLUSION

An analytical methodology for the determination of low molecular-weight aldehydes (C1-C7) in aqueous solution has been described. The work presented here in has demonstrated that headspace solid phase microextraction/ gas chromatographic analysis of PFBHA derivatives. Because of the good recoveries, relative standard deviation and sensitivity, the HS-SPME /GC/FID is considered to be an efficient technique for determination of low molecular weight aldehydes in aqueous solution. In addition, this technique is simple, solvent free and timesaving.

REFERENCES


